

Synthesis and Characterisation of Layered Hydroxy Anion Exchange Materials

Abstract

This thesis concerns the synthesis and characterisation of layered hydroxy anion exchange materials. The incorporation of rare-earth cations into these materials offers the potential to combine the optical, magnetic and catalytic properties of the lanthanides with the flexibility of intercalation hosts.

A review of the literature surrounding intercalation chemistry and materials is presented in **Chapter 1**. Here the synthesis, structure and anion exchange reactions of layered hydroxides and their applications in the fields of catalysis, separation science, polymer additives and biological storage and delivery are discussed.

Chapter 2 describes the hydrothermal synthesis and anion exchange capacity of new anion exchange host lattices containing the smaller lanthanide cations, with the composition $\text{Ln}_2(\text{OH})_5\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ ($\text{Ln} = \text{Y}, \text{Gd} - \text{Lu}$), with Gd marking a limiting cation radius. Anion exchange reactions are facile with a wide range of organic carboxylates and sulfonates and investigations into their selectivity and optical properties have been carried out. This family has also been expanded to include $\text{Ln}_2(\text{OH})_5\text{X} \cdot 1.5\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}; \text{Ln} = \text{Y}, \text{Dy}, \text{Er}, \text{Yb}$) and crystal structures for orthorhombic and monoclinic $\text{Yb}_2(\text{OH})_5\text{Cl} \cdot 1.5\text{H}_2\text{O}$ are reported.

The findings of a time-resolved *in situ* X-ray powder diffraction study form the basis of **Chapter 3**. Three different phases with the layer composition $[\text{Yb}_2(\text{OH})_5]^+$; $\text{Yb}_2(\text{OH})_5\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ $d = 9.2 \text{ \AA}$ (1), $\text{Yb}_2(\text{OH})_5\text{NO}_3 \cdot 2\text{H}_2\text{O}$ $d = 9.4 \text{ \AA}$ (2) and $\text{Yb}_2(\text{OH})_5\text{NO}_3 \cdot \text{H}_2\text{O}$ $d = 8.5 \text{ \AA}$ (3) were observed and shown to ultimately transform to a 3D structure $\text{Yb}_4\text{O}(\text{OH})_9\text{NO}_3$ $d = 8.0 \text{ \AA}$ (4). Single crystal structures are given for phases 2 and 3, and the structure of 4 has been refined. The effects of temperature and metal concentration on phase formation have been investigated and compared with *ex situ* results. A full kinetic analysis is presented including the activation energy for the formation of phase 2. The values extracted indicate that the mechanism of crystallisation is phase boundary controlled.

In **Chapter 4** the room temperature precipitation synthesis of a related family of anion exchange host lattices with the composition, $\text{Ln}_2(\text{OH})_5\text{NO}_3 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Y}, \text{Eu} - \text{Er}$) and MgAl layered double hydroxides incorporating the precious metals Ru and Pd are discussed.

Details of synthetic routes to the novel materials described and the methods of characterisation used are given in **Chapter 5**.

Acknowledgements

Firstly I would like to thank my supervisor Dr. Andrew Fogg for giving me the opportunity to work in his research group and for his help, guidance and advice over the past three years. A special mention has to go to my fellow long-term group member and office-mate Richard for always keeping me laughing and despairing in equal measure. Good luck to Jen our newest addition, I've enjoyed our random conversations in the lab and it's been good having you around, keep at it! Thanks to previous students Lauren, Leslie and Sheena for all their hard work – especially Lauren for making my first year so enjoyable and for letting me wear that beautiful blue dress for the day.

To those Lab A affiliates who shared the good, the bad and slightly-charred times; (particularly those that stuck it out to the end) Jamie with his tails of crowd-surfing injuries and knowledge of obscure Indie bands and Romain, the spikey Frenchman who always kept us guessing – we survived! Also to past members Mike, Jean-Noel, Jorge and honorary weird scientist-type Colin for making the lab a fun place to be. Particularly enjoyable were the strange music choices, the ramblings of tea breaks, the periods of quiet contemplation and the memorable extended pub lunches.

Thanks to Steve Apter at the department's elemental analysis service for running endless CHNs and ICPs. Recognition must go to Drs. Calum Dickinson and Simon Romani for their help and advice during my TEM training (the time always passed quicker with Calum around). I'm also indebted to Dr. Mathieu Allix and Gary Evans for their TEM and SEM images, often run at short notice. Cheers, or perhaps, merci beaucoup to Dr. Romain Heck for helpful discussions during the course of the luminescence work and for fluorimeter training. Our time at Daresbury deserves a particular mention, for technical help at Station 16.4 thanks to Dr. Dave Taylor and of course who could forget the culinary expertise that was exercised at the canteen... A big thank you to Dr. Tim Prior for his hard work at Station 9.8 with some extremely small crystals, your efforts are very much appreciated.

Finally and most of all I'm eternally grateful to Mum, Dad and Cheryl who've supported me in every way imaginable throughout these three years and indeed through my seemingly eternal student status. Special credit has to go to Mike for living with me during this writing-up period, it can't have been easy. Thanks so much, I can honestly say I couldn't have done it without you lot.

Abbreviations

AQDS	2,6-Anthraquinonedisulfonate
BDA	Benzenedicarboxylate
EDS	Energy-dispersive X-ray spectroscopy
EDXRD	Energy-dispersive X-ray diffraction
FTIR	Fourier transform infra-red
HDS	Hydroxy double salt
LDH	Layered double hydroxide
LRH	Layered rare earth hydroxide
NDS	2,6-Naphthalenedisulfonate
NMR	Nuclear magnetic resonance
NZA	Zinc nickel hydroxy acetate
SAED	Selected area electron diffraction
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UV	Ultra-violet
XRD	X-ray diffraction
ZCA	Zinc copper hydroxy acetate
ZHA	Zinc hydroxy acetate

Contents

Abstract	<i>i</i>
Acknowledgements	<i>ii</i>
Abbreviations	<i>iii</i>
Chapter 1: Introduction	1
1.0 Intercalation Chemistry	1
1.1 Intercalation Materials	3
1.2 Layered Hydroxide Anion Exchange Materials	5
1.3 Structure	5
1.3.1 Layered Double Hydroxides (LDHs)	5
1.3.2 Hydroxy Double Salts (HDSs)	9
1.3.3 Hydroxy Nitrate Salts and Layered Rare Earth Hydroxides (LRHs)	11
1.4 Synthesis	12
1.4.1 Layered Double Hydroxides (LDHs)	13
1.4.2 Hydroxy Double Salts (HDSs)	16
1.4.3 Hydroxy Nitrate Salts and Layered Rare Earth Hydroxides (LRHs)	16
1.5 Anion Exchange	18
1.5.1 Intercalation of Simple Inorganic Anions	19
1.5.2 Intercalation of Complexes	19
1.5.3 Intercalation of Organic Anions	20
1.6 Applications of Layered Hydroxides	21
1.6.1 Catalysis	22
1.6.2 Separation Science	23

1.6.3	Polymer Additives	25
1.6.4	Biological Storage and Delivery	27
1.7	Aims	30
1.8	References	31

Chapter 2: New Anion Exchangeable Layered Lanthanide Hydroxides: Their Synthesis, Characterisation and Properties **41**

2.0	Introduction	41
2.1	Scope of Chapter	43
2.2	$\text{Ln}_2(\text{OH})_5\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ (Ln = Y, Gd – Lu) – A Novel Family of Anion Exchange Intercalation Hosts	43
2.2.1	Synthesis and Characterisation	43
2.2.2	Anion Exchange Reactions	50
2.2.3	Orientation of Guest Anions	55
2.2.4	Comparison with other LRH Materials	57
2.3	Properties of the $\text{Ln}_2(\text{OH})_5\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ Materials	58
2.3.1	Competitive Anion Exchange Reactions	58
2.3.2	Optical Properties	69
2.4	Hydroxyhalide Anion Exchange Materials $\text{Ln}_2(\text{OH})_5\text{X} \cdot 1.5\text{H}_2\text{O}$ (X = Cl, Br; Ln = Y, Dy, Er, Yb)	74
2.4.1	Synthesis and Characterisation	74
2.4.2	Anion Exchange Reactions	83
2.5	Conclusions	86
2.6	Recent Developments	87
2.7	References	89

Chapter 3: *In situ* Energy Dispersive X-ray Diffraction Study: Converting Layered and Framework Ytterbium Hydroxide Phases **93**

3.0	Introduction	93
-----	--------------	----

3.1	<i>In situ</i> Energy Dispersive X-ray Diffraction	95
3.2	Apparatus	97
3.3	Solid State Kinetics	100
3.3.1	Avrami-Erofe'ev	102
3.4	Previous Uses	104
3.5	Scope of Chapter	107
3.6	Results and Discussion	108
3.7	Phase Isolation and Characterisation	116
3.7.1	Phase 1: $\text{Yb}_2(\text{OH})_5\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ ($d = 9.2 \text{ \AA}$)	116
3.7.2	Phase 2: $\text{Yb}_2(\text{OH})_5\text{NO}_3 \cdot 2\text{H}_2\text{O}$ ($d = 9.4 \text{ \AA}$)	119
3.7.3	Phase 3: $\text{Yb}_2(\text{OH})_5\text{NO}_3 \cdot \text{H}_2\text{O}$ ($d = 8.5 \text{ \AA}$)	125
3.7.4	Phase 4: $\text{Yb}_4\text{O}(\text{OH})_9\text{NO}_3$ ($d = 8.0 \text{ \AA}$)	133
3.7.5	Anion Exchange	139
3.8	Kinetic Analysis	141
3.8.1	Temperature Dependency Experiments	141
3.8.2	Yb Concentration Experiments	149
3.9	Conclusions	152
3.10	References	153

Chapter 4: Precipitation Synthesis as a Route to Lanthanide Hydroxynitrate Anion Exchange Materials and Layered Hydroxides Containing Precious Metals **156**

4.0	Introduction	156
4.1	Scope of Chapter	158
4.2	Precipitation Synthesis of Lanthanide Hydroxynitrate Anion Exchange Materials; $\text{Ln}_2(\text{OH})_5\text{NO}_3 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Y}, \text{Eu} - \text{Er}$)	159
4.2.1	Results and Discussion	159
4.2.2	Anion Exchange Reactions	164

4.3	Synthesis and Characterisation of LDHs Containing Precious Metals	168
4.3.1	Results and Discussion	168
4.3.1.1	Ruthenium containing MgAl-NO ₃ LDHs	169
4.3.1.2	Ruthenium containing MgAl-Cl LDHs	175
4.4	Summary	178
4.5	References	179
Chapter 5: Experimental Details		182
5.0	Introduction	182
5.1	Analytical Techniques	182
5.1.1	Elemental Analysis	182
5.1.2	Powder X-ray Diffraction	182
5.1.3	Thermogravimetric Analysis	183
5.1.4	Transmission Electron Microscopy	183
5.1.5	Scanning Electron Microscopy	183
5.1.6	Fourier Transform Infra red Spectroscopy	184
5.1.7	Solution NMR Spectroscopy	184
5.1.8	Ultraviolet-Visible Spectroscopy	184
5.1.9	Fluorescence Spectroscopy	184
5.2	Synchrotron Radiation Studies	185
5.2.1	<i>In situ</i> Energy Dispersive X-ray Diffraction	185
5.2.2	Single Crystal X-ray Diffraction	188
5.3	Experimental Details for Chapter 2	188
5.3.1	Synthesis of Ln ₂ (OH) ₅ NO ₃ ·xH ₂ O (Ln = Y, Gd-Lu) Phases	188

5.3.2	Anion Exchange Reactions	189
5.3.3	Synthesis of Carboxylic Acid Sodium Salts	189
5.3.4	Synthesis of $[\text{Ln}_4(\text{OH})_{10}(\text{H}_2\text{O})_4]\text{A}_n$ (Ln = Dy, Er)	189
5.3.5	Selective Anion Exchange Reactions	190
5.3.6	Synthesis of $\text{Ln}_2(\text{OH})_5\text{X}\cdot 1.5\text{H}_2\text{O}$ (Ln = Y, Dy, Er, Yb; X = Cl, Br) Phases	190
5.3.7	Synthesis of Mixed Metal Hydroxides (Yb/Eu, Yb/Gd and Eu/Er)	190
5.4	Experimental Details for Chapter 3	191
5.4.1	<i>In situ</i> EDXRD Experiments	191
5.4.2	Conditions for Phase Isolation	191
5.5	Experimental Details for Chapter 4	192
5.5.1	Synthesis of $\text{Ln}_2(\text{OH})_5\text{NO}_3\cdot \text{H}_2\text{O}$ (Ln = Y, Eu–Er)	192
5.5.2	Anion Exchange Reactions of $\text{Ln}_2(\text{OH})_5\text{NO}_3\cdot \text{H}_2\text{O}$ (Ln = Y, Eu–Er)	192
5.5.3	Synthesis of Ru doped MgAl LDHs	193
5.5.3.1	Attempted Hydrothermal Synthesis	193
5.5.3.2	Attempted Synthesis by Slow Growth Method	193
5.5.3.3	Attempted Synthesis by Vapour Diffusion Method	193
5.5.3.4	Coprecipitation-Urea method	194
5.5.3.5	Coprecipitation method	194
5.6	References	194
	Appendices	196